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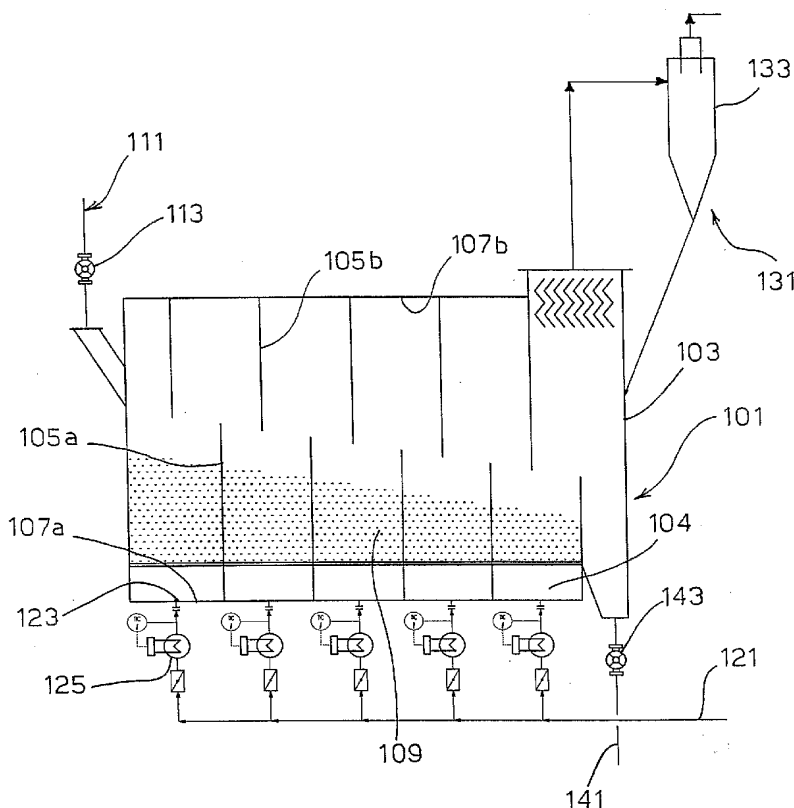
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**(54) Title:** REACTOR AND PROCESS FOR SOLID PHASE CONTINUOUS POLYMERISATION OF POLYETHYLENE TEREPHTHALATE (PET)



**(57) Abstract:** A reactor and a process for solid phase continuous polymerisation of polyethylene terephthalate (PET) in order to achieve an increase of the intrinsic viscosity (I.V.) of a low molecular weight PET pre-polymers flow, wherein the formation of a plurality of fluidised stages in series (109; 309) is provided, being said PET pre-polymers flow fed into said fluidised stages in series (109; 309) and being an inert gas flow fed either in cross-flow or in counter-current flow with respect to said PET pre-polymers flow.



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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

REACTOR AND PROCESS FOR SOLID PHASE CONTINUOUS POLYMERISATION  
OF POLYETHYLENE TEREPHTHALATE (PET)

DESCRIPTION

The present invention relates to a reactor and a process for  
5 solid phase continuous polymerisation of polyethylene  
terephthalate (PET).

More exactly, the present invention relates to a reactor and a  
process for solid phase continuous polymerisation of  
polyethylene terephthalate (PET) in order to achieve an  
10 increase of the intrinsic viscosity (I.V.) of a low molecular  
weight PET pre-polymers flow.

Generally, PET manufacturing process includes four steps:  
esterification, pre-condensation, finishing step and solid  
phase polymerisation.

15 In the past, PET manufacturing process was carried out by  
transesterification of dimethyl terephthalate (DMT) with  
ethylene glycol (EG) while direct esterification of purified  
terephthalic acid (PTA) with ethylene glycol (EG) is nowadays  
well-established, whose advantages mainly reside both in its  
20 cost effectiveness and in its higher reaction rate.

Ethylene glycol (EG) and oligomers are present among the by-  
products at the end of the reaction.

Ethylene glycol (EG) is usually recycled in feed at the  
beginning of the process, thus increasing the overall yield;  
25 the oligomers have to be removed and then be disposed of or,  
alternatively, recycled to continue increasing their

polymerisation grade.

It is known that the oligomers in the field of interest, i.e. within the PET manufacturing processes and, more generally, within the polyester ones, are normally molecules having 2, 3  
5 or maximum 4 polymerisation grade, at gaseous state at high temperature conditions and at liquid state at temperatures lower than  $120 \div 150$  °C.

Said oligomers are present at gaseous state at the end of the reaction, but tend to condense on the colder metal surfaces of  
10 piping/fittings they pass through; once condensed, they tend to produce sticky mixture together with finest dusts that are not removed by cyclone separation systems usually provided downstream the PET manufacturing plants.

Such sticky mixture settles onto the pipes walls and  
15 progressively reduces the flow areas thereof, until causing the whole system shutdown in case it is not properly removed during maintenance operations.

In consequence of what above described, it becomes evident that the oligomers removal from the gaseous flow exiting the plant  
20 is essential.

The conventional melt-phase polymerisation processes routinely use the first three steps previously mentioned, i.e. esterification, pre-condensation and finishing step, to produce so-called pre-polymers for the subsequent solid phase  
25 polymerisation.

Solid phase polymerisation is a thermal treatment process that

allows to increase the molecular weight of a polymer at different levels, depending on the kind of final product that it is wanted to be obtained.

It is known that the molecular weight of a polymer can be  
5 measured by the measure of its intrinsic viscosity I.V. (Intrinsic Viscosity).

It is also known that the increase of the molecular weight of a polymer can be achieved by subjecting low molecular weight polymers (pre-polymers), preferably under granular form, to a  
10 solid phase continuous polymerisation step on fluidised bed.

Such process further allows to provide polymers with low acetaldehyde content, content that must be lower than 1 p.p.m. for the manufacturing of PET bottles intended for food use.

The pre-polymers fed to the solid phase polymerisation step can  
15 be under the form of completely amorphous pellets or partially crystallised pastilles.

Amorphous PET pellets are thermally stable only up to the glass transition temperature, which is about 80°C; however, the temperature of the solid phase polymerisation process is higher  
20 than 200°C.

By subjecting amorphous PET pellets to a heating phase as well as to a temperature maintaining phase above the glass transition temperature, a progressive crystallisation of the polymeric bulk is achieved, by hardening the polymer matrix  
25 inside pellets themselves, so achieving thermal stability up to temperature values close to the onset (about 235°C) of melting

point.

Due to this reason, pre-crystallisers and crystallisers are generally necessary plant units upstream the conventional solid phase polymerisation reactor.

- 5 The purpose of the crystallisation step prior to solid phase polymerisation is to prevent the agglomeration of the granules during the polymerisation process, especially at the highest temperatures.

As a matter of fact, it is known that in nowadays employed  
10 industrial solid phase polymerisation plants, the granules agglomeration phenomenon frequently happens; this problem is particularly evident during PET solid phase continuous moving bed polymerisation for producing bottles intended for food use, when polymerisation is carried out at temperatures above the  
15 amorphous PET pre-polymer glass transition temperature, but below the melting point.

According to the conventional processes today available and employed for solid phase polymerisation, the PET pre-polymer (crystallised or partially crystallised) is fed at the top of a  
20 vertical moving or static bed reactor for solid phase polymerisation, in which the pre-polymer moves downwards by gravity in contact with an inert gas stream.

According to known prior art, the inert gas primarily functions to remove unwanted by-products, in particular ethylene glycol,  
25 acetaldehyde and water vapour, which are generated during polymerisation, while PET gradually moves towards the bottom of

the vertical reactor.

In general, there are three important requisites that are to be met for correct operation of a continuous solid phase polymerisation process.

5 First, a steady and uninterrupted flow of PET granules must be maintained.

As a consequence, it is highly important that agglomeration of PET granules is avoided, since it would impede the smooth flow of granules and it would make difficult the discharge of the  
10 product from the reactor, thereby causing the plant control losing.

Secondly, a suitable combination of residence time and temperature of granules in the reactor is required to achieve the desired molecular weight, which is measurable, as indicated  
15 above, in terms of intrinsic viscosity I.V..

Since reaction rate increases with temperature increase, and I.V. increases with residence time increase in the reactor, desired I.V. can be attained either by using a relatively long residence time, with a relatively low temperature, or a  
20 relatively short residence time with a relatively high temperature.

However, the ideal combination of residence time and temperature must be chosen taking into account the first of the requisites indicated above, i.e. the need to maintain a linear  
25 flow, thereby avoiding the granules agglomeration phenomenon.

Third, the flow regime of PET granules processed inside the

solid phase polymerisation reactor, must be as close as possible to the ideal plug-flow behaviour; this way all PET granules passing through the reactor undergo the same conditions of treatment and a narrow molecular weight distribution in the obtained product and, more in general, a narrow distribution of polymerised granules final attributes, which is a key factor for the required performance during subsequent high I.V. PET product processing/converting steps, will be achieved.

As regards the first requisite, that is the need to avoid the PET granules agglomeration, it is to be said that this phenomenon is mainly affected by temperature, granules size, bed height, granules flow velocity within the reactor and PET morphology.

PET granules, initially moving freely in a moving bed can stick and clot if, for instance, temperature or bed height increases or if cross-sectional velocity decreases.

At solid phase polymerisation conditions, PET is only partially crystallised and, as a consequence, such a PET is not a rigid body, but it is rather a slightly sticky body.

Since the PET tendency to become sticky increases with temperature increase, the agglomeration tendency also increases with temperature increase.

A fixed bed of PET granules held motionless inside a solid phase polymerisation vertical, cylindrical reactor is taken into account.



Under these conditions, at polymerisation temperature and under pressure due to the weight of the PET granules bed, granules to be polymerised creep into one another at contact points and, in time, polymer granules will tend to agglomerate and form larger lumps.

The most effective way to prevent lumping is to constantly renew the intergranular contact areas, so that polymer granules do not have a chance to creep into one another.

This purpose is achieved by maintaining a constant flow of polymer granules at sufficiently high velocity.

Since agglomeration tendency increases with the increase of the specific surface area (area per unit mass) or, more precisely, with the increase of the specific contact area of polymer granules, it also increases with the decrease of the size of polymer granules.

A reduced granules size contributes to accelerate the polymerisation process, however, on the other hand, the agglomeration tendency of polymer granules increases.

In presence of small size granules it is therefore required to counterbalance the increased agglomeration tendency with a temperature decrease, which, on the other hand, brings the final values of the process rate back to the typical ones for larger size granules treated at a higher temperature.

Furthermore, if the particle size is reduced below certain limits, agglomeration occurs practically at any temperature.

In a static or moving bed situation, the compaction pressure

undergone by polymer granules is approximately proportional to the weight of the polymer granules inside the bed which, in its turn, is proportional to the bed height above the granules; therefore, polymer agglomeration tendency is highest at the bottom of the bed and lowest at the top.

From what above mentioned it results that polymer lumps start generally to form near the bottom of the bed; for this reason there is a practical limit on the bed height of a solid phase polymerisation reactor.

At a sufficiently high flow velocity, polymer granules change their positions relative to each other (by sliding, for instance) and lumps formation is thereby prevented.

Since the change rate of polymer granules contact areas and the reduction of bed bulk density increase with the increase of the granules velocity, polymer agglomeration tendency inside the reactor decreases with the increase of the granules cross-sectional velocity.

For each combination of reactor temperature, bed height, and particle size, there exists a minimum granules velocity necessary to prevent agglomeration.

For each given size and shape of polymer granules, the minimum velocity to prevent agglomeration increases with the increase of temperature and bed height.

In case polymerisation temperature increases or in case bed height increases, a higher velocity has to be used; in case, for instance, of commercial scale vertical reactors, with

outputs up to 300 metric tons per day and which are conventionally 18 to 22 meters high, a velocity of at least 2 meters per hour is generally required.

A well designed solid phase polymerisation commercial scale  
5 plant must be capable of continuously producing outputs having intrinsic viscosity I.V. in compliance with the required specification at a sufficiently high throughput.

The currently used plants employ single or multiple vertical cylindrical reactors 10 to 30 meters high; in those plants the  
10 reactor is operated at a temperature of 200 to 230 °C and at a granules moving velocity of 1.00 to 2.52 meters per hour.

Within the above-mentioned ranges of temperature, bed height, and granules velocity, the choice to achieve a product with the desired I.V. can be made.

15 These conventional currently used plants allow to produce PET having an I.V. of 0.72 to 0.86 dl/g, using PET pre-polymers with an I.V. of 0.55 to 0.65 dl/g; these conventional plants can increase polymer I.V. by about 0.12 - 0.25 dl/g.

Amorphous PET granules have intrinsic viscosity values  
20 generally comprised in the range  $0.57 \div 0.62$  dl/g; the reaction time necessary to achieve final I.V. value in the range  $0.72 \div 0.85$  dl/g, required for the most bottle manufacturing applications, is of  $12 \div 18$  hours.

Usually, PET I.V. is brought to the above-mentioned values,  
25 commercially required for bottle manufacturing, through polymerisation processes carried out in continue solid phase

vertical reactors, in which solid bed of PET granules moves downwards by gravity.

For some specific applications, for instance PET pre-polymers polymerisation for standard bottle manufacturing, characterised  
5 by initial I.V. values of 0.25 - 0.45 dl/g, it is necessary to increase said I.V. by more than 0.25 dl/g.

This result is hardly achievable and often it is not achievable in a conventional plant using said vertical reactors.

In a conventional process, there are two ways to raise the  
10 product I.V.; namely, to increase the reactor temperature or to increase the granules residence time inside the reactor.

The residence time inside the reactor is constrained by bed height and by granules velocity; it can be increased either by increasing bed height or by decreasing granules velocity.

15 Increasing the reactor diameter allows an increase in the throughput rate, but not in residence time at constant granules velocity.

On the other hand, if reactor temperature is raised to increase the final product I.V., polymer agglomeration tendency will  
20 consequently increase.

To prevent polymer agglomeration, bed height has to be decreased or granules velocity has to be increased. However, both these modifications reduce residence time inside the reactor and nullify the effect of the temperature increase.

25 Alternatively, if the residence time inside the reactor is increased either by increasing the bed height (assuming the

reactor is sufficiently tall) or by reducing the granules velocity, an increase of the polymer agglomeration tendency is caused.

To prevent the agglomeration phenomenon, the reactor  
5 temperature must be lowered and this once again nullifies the effect of the residence time increase on the product final I.V..

These constraints limit the ability of conventional plants, which use single or multiple vertical reactors, to increase the  
10 polymer intrinsic viscosity I.V..

A similar situation is encountered when a commercial scale plant with a capacity above 360 metric tons per day has to be designed for conventional continuous solid phase polymerisation processes.

15 In fact, in a conventional process, there are two ways to reach high plant production capacity: again by increasing the reactor temperature or by increasing the product volume ("hold-up") in the reactor.

As far as drawbacks due to the temperature increase are  
20 concerned, the same above described issues have to be considered.

On the other hand, the product volume ("hold-up") of PET granules in the reactor is constrained by bed height, reactor diameter and granules velocity.

25 If the product volume ("hold-up") is increased either by increasing bed height or reactor diameter, or by decreasing

granules velocity, polymer agglomeration tendency will increase too.

Thus, these constraints limit the maximum capacity of conventional solid phase polymerisation processes, which use one or more vertical cylindrical reactors.

Nowadays, growing PET demand has given rise to a need for solid phase polymerisation processes by means of which it is possible to achieve a higher increase of PET molecular weight and a higher production capacity, typically higher than 300 metric tons per day on single plant.

One of the drawbacks of the plants according to the known prior art is due to the considerable vertical size of the plant structure due to the presence of the pre-crystallisation unit, which is stacked onto the crystallisation unit, stacked in its turn onto the solid phase polymerisation reactor.

A second drawback is represented by the long residence time, inside the conventional reactor, required to achieve the desired I.V. increase starting from amorphous pre-polymers; for example, to get from an I.V. of 0.60 dl/g to that of the final product, which is equal to 0.80 dl/g in the case of application in the manufacturing of standard bottles intended for food use, an average residence time equal to 15 hours is needed.

Such drawback is substantially due to two reasons: the fact that the solid phase polymerisation kinetic is linked to the reaction gaseous products diffusivity from the granules core to their outside and the fact that the pre-crystallisation and

crystallisation steps, which are mandatory to secure enough flowability to the granules in a conventional moving bed solid phase polymerisation reactor, limit the polymeric matrix portion able to react, being the only non-crystalline portion to be involved in the reaction. A known solution to the above-mentioned problems consists in the use of PET sand of spherical granules having a sufficiently small size (typically  $100 \div 200$   $\mu\text{m}$ ) and of a great amount of inert gas in the reactor.

Thanks to these expedients the pre-crystallisation and crystallisation steps have been avoided, the reaction time has been reduced and the solid phase polymerisation reactor acquires lower size.

The aforesaid solution is nevertheless not optimal from the point of view of cost, of reactor size, of the achievable I.V., of I.V. distribution and of the reaction time.

A first purpose of the present invention is therefore to provide an improved reactor for solid phase continuous polymerisation of polyethylene terephthalate (PET) in order to achieve an increase of the intrinsic viscosity I.V. that allows to overcome the constraints of the processes known so far, that is to reduce the process time and the reactor size.

A further purpose of the invention is therefore to provide a reactor and a process for PET solid phase polymerisation that allows to achieve high production capacities.

In the solid phase polymerisation plants also the gas flow-rate has to be sufficient to effectively remove the reaction by-

products; as a matter of fact, a gas excess results in higher costs both for its supply and for its regeneration and disposal.

Therefore, a further purpose of the invention is to provide a  
5 reactor and a process for solid phase polymerisation that allows to reduce the costs due to the gas employment.

These and other purposes are achieved with the reactor and the process as claimed in the attached claims.

Advantageously, thanks to the provision of a plurality of  
10 fluidised stages to carry out the solid phase continuous polymerisation of a low molecular weight PET pre-polymers flow, a polymerisation up to the desired I.V. value in a moderate reaction time by using a compact reactor is achieved.

Advantageously, the reactor and the process according to the  
15 invention further allow to avoid unwanted agglomeration phenomena and other side effects even achieving higher molecular weight increases of the treated PET when compared with the ones achievable with the conventional processes of the known prior art.

20 The reactor and the process according to the invention further allows to achieve a high degree of plug-flow ("plug-flow") and, consequently a high homogeneity and uniformity of the final product.

Advantageously, moreover, the reactor according to the  
25 invention allows to achieve higher production capacities when compared with the plants exploiting the conventional processes.



Always according to the invention is furthermore possible to advantageously achieve a reduction of energy consumption, thanks to the decreased overall process  $\Delta P$  required for the gas with respect to conventional processes.

5 The optimal number of fluidised stages was ascertained experimentally, by employing both a model formed by single fluidised bed reactors arranged in series, and a fluidised reactor model within which a plurality of fluidised stages is generated.

10 The invention will be now described more in detail with particular reference to the attached drawings, provided by way of not limiting example, wherein:

- Figure 1A is a diagram of a first embodiment of the invention;

15 - Figure 1B is a diagram according to an alternative form of the embodiment of the invention shown in Figure 1A;

- Figures 2A to 2E show the curves of some quantities that are significant for achieving the purposes of the invention;

20 - Figure 3A is a diagram of a second embodiment of the invention;

- Figure 3B is a diagram according to an alternative form of the embodiment of the invention shown in Figure 3A.

With reference to Figure 1A a reactor 101 comprising a horizontally arranged casing 103, having a substantially parallelepiped shape, is shown.

25

A first feeding line 111, equipped with a device 113 (for

example, a rotating volumetric distributing apparatus) to regulate the flow-rate of fed amorphous PET pre-polymer and to prevent gas leakage, is provided to feed a continuous low molecular weight PET pre-polymers flow (preferably a PET sand  
5 having granules with size in the range  $100 \div 200 \mu\text{m}$ ) to the top of reactor 101.

A second gas feeding line 121 is provided to feed through supply valves 123 an inert gas flow, preferably nitrogen, from the bottom into the reactor 101, in cross-flow with respect to  
10 the pre-polymer flow inside the reactor 101.

A circuit 131 connected to the reactor 101 is provided to purify the gas and to recover pre-polymer particles by means of a proper separator 133, such as a cyclone; solid particles dragged by the gas exiting the reactor 101 and recovered by  
15 means of the separator 133, are then recycled to the reactor 101.

According to an alternative form, shown in Figure 1B, the gaseous flow containing, among others, ethylene glycol and oligomers, is forced to preventively pass through an  
20 appropriate separation device 135, such as for example a condensation separator, wherein ethylene glycol and oligomers are recovered at the liquid state and then recycled to the esterification reactor RE that is located upstream the manufacturing plant to carry out the primary reaction of the  
25 PET manufacturing process.

The gas without solid particles leaving the separator 133 from

its head, is conveyed to a following purification unit (not shown) wherein all the residual hydrocarbons that are present in the gaseous flow are removed by means of known techniques, for example the catalytic oxidation; said gas flow is then  
5 subjected to drying, for example for adsorption on molecular sieves, and then recycled to the solid phase polymerisation reactor 101 as fluidising and stripping means of the reaction gaseous by-products.

A third discharging line 141, equipped with a device 143 (for  
10 example, a rotating volumetric distributing apparatus) to discharge the PET after solid phase polymerisation and to prevent gas leakage, is provided to discharge the polymerised product by being inferiorly connected to the bottom of the reactor 101.

15 Advantageously, according to the invention, inferior vertical walls 105a, secured to the base of the reactor 101, and superior vertical walls 105b, secured to the ceiling of the reactor 101, are provided inside the reactor 101.

Said walls 105a and 105b are preferably formed from metal  
20 plates secured, for example by welding, respectively to the base 107a of the casing 103 and to the ceiling 107b of the casing 103.

Moreover, said walls 105a have decreasing height in the polymer flow advancing direction, while said walls 105b have increasing  
25 height in the same direction in order to prevent that the polymer flow could "skip" one or more fluidised stages 109.

Said walls 105a and 105b are further spaced so as to create between them corresponding fluidised stages 109, which are generated thanks to the action of the opposite direction gas flow coming from the holed bottom 104 of the casing 103.

5 Advantageously, according to the invention, said supply valves 123 are in such a number and arranged in such a way to generate a sufficient gas flow in correspondence with each fluidised stage 109.

Moreover, each supply valve 123 or each supply valves 123 set  
10 associated to the same fluidised stage, is equipped with a heating device 125 suitable for bringing at the desired temperature the inert gas flowing through the bottom 104 of the reactor 101.

This way, still according to the invention, each fluidised  
15 stage 109 can receive inert gas at the optimal temperature chosen in dependence of the polymerisation degree reached inside the reactor 101 so achieving a non-isothermal process.

According to the invention, the pre-polymers flow, coming from the feeding line 111, passes through a plurality of fluidised  
20 stages 109, prior to reach the discharge line 141 located downstream the last fluidised stage.

During crossing reactor 101, pre-polymers are conveniently polymerised by achieving the desired intrinsic viscosity I.V..

According to the invention, the intrinsic viscosity value  
25 attained at the end of the reaction depends on the number of the fluidised stages.

As it will become evident from the following description, said fluidised stages are preferably in the number of five.

In order to optimise the number of fluidised stages to be created inside the reactor, some simulations have been carried  
5 out by employing as model a plant formed by a plurality of single fluidised bed reactors arranged in series.

With reference to Figures 2A and 2B, the trend of the average I.V. final value with respect to the number of reactors of said plant model is shown.

10 Figure 2A refers to the case wherein pre-polymers having an initial I.V. of 0.30 dl/g are used, with overall residence time of three hours and with reaction temperature inside each reactor of 210°C (curve T1), 220°C (curve T2) and 230°C (curve T3).

15 As it will be noticed by examining the trend of the three curves T1, T2 and T3, the number of single fluidised bed reactors beyond which the final I.V. increase is no more significant is about five.

Figure 2B refers to the case wherein the overall residence time  
20 is of five hours and the steady reaction temperature inside each reactor is of 220°C, by using pre-polymers having an initial I.V. of 0.20 dl/g (curve V1), 0.26 dl/g (curve V2) and 0.30 dl/g (curve V3).

As it will be noticed by examining the trend of the three  
25 curves V1, V2 and V3, the number of single fluidised bed reactors beyond which the final I.V. increase is no more

significant is about five.

With reference to Figure 2C, the trend of the average I.V. final value with respect to the reaction time required to attain the desired polymerisation is shown.

5 Figure 2C refers to the case wherein pre-polymers having an initial I.V. of 0.30 dl/g are used, with reaction temperature of 230°C and with a number of fluidised stages of one (curve S1), five (curve S2) and twenty (curve S3).

As it will be noticed by examining the trend of the three  
10 curves S1, S2 and S3, the number of fluidised stages beyond which the reaction time reduction is no more significant is about five.

Figure 2D refers to the case wherein pre-polymers having an initial I.V. of 0.30 dl/g are used, with a plant having five  
15 fluidised stages and with reaction temperature of 210°C (curve T4), 220°C (curve T5) and 230°C (curve T6).

As it will be noticed by examining the trend of the three curves T4, T5 and T6, in a plant provided with five fluidised stages, meaning to achieve a final intrinsic viscosity I.V.  
20 value of about 0.84 dl/g, the more the reaction temperature is high the more the reaction time reduction is significant.

Figure 2E refers to the case wherein a plant having five fluidised stages is used, with temperature of 230°C and by using pre-polymers having an initial I.V. of 0.20 dl/g (curve  
25 V4) and 0.30 dl/g (curve V5).

As it will be noticed by examining the trend of the two curves

V4 and V5, in a plant provided with five fluidised stages, meaning to achieve a final intrinsic viscosity I.V. value of about 0.84 dl/g, a moderate increase of the pre-polymer initial I.V. results in a considerable reduction of the reaction time.

5 With reference to Figure 3A a second embodiment of the invention is shown, wherein a reactor 301 comprising a vertically arranged casing 303, having a substantially cylindrical shape, is provided.

A first feeding line 311, equipped with a device 313 (for  
10 example, a rotating volumetric distributing apparatus) to regulate the flow-rate of fed amorphous PET pre-polymer and to prevent gas leakage, is provided to feed, from the top of reactor 301, a continuous low molecular weight PET pre-polymers flow, preferably a PET sand having granules with size in the  
15 range  $100 \div 200 \mu\text{m}$ .

A second gas feeding line 321 is provided to feed through supply valves 323 an inert gas flow, preferably nitrogen, from the bottom into the reactor 301, in counter-current flow with respect to the descending pre-polymer flow inside the reactor  
20 301.

A circuit 331 connected to the top of the reactor 301 is provided to purify the gas and to recover pre-polymer particles by means of a proper separator 333, such as a cyclone; solid particles dragged by the gas exiting the reactor 301 and  
25 recovered by means of the separator 333, are then recycled to the reactor 301.

According to an alternative form, shown in Figure 3B, the gaseous flow containing, among others, ethylene glycol and oligomers, is forced to preventively pass through an appropriate separation device 335, such as for example a  
5 condensation separator, wherein ethylene glycol and oligomers are recovered at the liquid state and then recycled to the esterification reactor RE that is located upstream the manufacturing plant to carry out the primary reaction of the PET manufacturing process.

10 The gas without solid particles leaving the separator 333 from its head, is conveyed to a following purification unit (not shown) wherein all the residual hydrocarbons that are present in the gaseous flow are removed by means of known techniques, for example the catalytic oxidation; said gas flow is then  
15 subjected to drying, for example for adsorption on molecular sieves, and then recycled to the solid phase polymerisation reactor 301 as fluidising and stripping means of the reaction gaseous by-products.

A third discharging line 341, equipped with a device 343 (for  
20 example, a rotating volumetric distributing apparatus) to discharge the PET after solid phase polymerisation and to prevent gas leakage, is provided to discharge the polymerised product by being inferiorly connected to the bottom of the reactor 301.

25 Advantageously, according to the invention, almost horizontal shelves 305 are provided inside the reactor 301.



Said shelves 305 are preferably formed from holed metal plates secured, for example by welding, to the internal wall 307 of the casing 303 so to extend substantially up to the centre line of the chamber created inside the casing 303.

- 5 Said shelves 305 are further preferably alternately arranged so to define, inside the reactor 301, an obligatory path that forces the pre-polymers flow to pass through at least two or more plates on which, thanks to the action of the opposite direction gas flow, corresponding fluidised stages 309 are thus  
10 generated.

According to the invention, the pre-polymers flow, coming from the feeding line 311, passes through a plurality of fluidised stages 309, prior to reach the reactor bottom and to be removed through the discharge line 341.

- 15 During crossing reactor 301, pre-polymers are conveniently polymerised by achieving the desired intrinsic viscosity I.V..  
According to the invention, the intrinsic viscosity value attained at the end of the reaction depends on the number of the fluidised stages.

- 20 As it is evident from the preceding description, said fluidised stages are preferably in the number of five.

With reference to the embodiment of Figure 1A, three carrying out examples are hereinafter described.

#### Example 1

- 25 Some tests with "PET sand" have been carried out in a pilot plant comprising a fluidised reactor 101 having five stages in

series, of parallelepiped shape.

Downstream the reactor, after the device 143 that in this example was a gas-tight rotating volumetric distributing apparatus device, a cooling unit of the (single stage) fluidised bed type was provided wherein air has been used as heat transferring and fluidising medium.

The solid phase polymerisation reactor 101, as already said, is a multistage (five stages arranged in series) fluidised reactor having parallelepiped shape, the base being 1,400 mm x 500 mm (gas distribution plate total surface) and the height being 3,200 mm, wherein the solid is fed at a end of the long side and the same progressively reacts by overflowing from a stage to the following one according to modes comparable to that of a fluid, and wherein the fluidising, heat transferring and gaseous reaction by-products removing gas is fed in cross-flow with respect to the solid phase.

The five stages with same volumes, completely independent from the point of view of both the gas fluid-dynamics and the solid one, are obtained by means of dividing walls 105a having decreasing height (respectively 2,000, 1,900, 1,800, 1,700 and 1,600 mm).

To prevent that the "PET sand" could "skip" one or more stages, close to the centre line of each stage a descending deflector (not shown) has been inserted, having an aperture in the top portion, said aperture being finalised to allow the removal of the gas exiting the single stages avoiding an acceleration of

the gas itself close to the overflows.

Each stage receives from the bottom the hot gas, through a distribution plate formed by a sintered steel plate, whose porosity is of 6.2% and which assures a  $\Delta P$  of about 50 mbar, so  
5 to guarantee a uniform distribution of the gas itself.

Each stage, as aforesaid, has a dedicated gas feeding circuit that is formed by a butterfly valve for flow-rate regulation, an electric heater for gas temperature control and a "settling chamber" onto which the above-mentioned gas distribution  
10 sintered plate is placed.

After having performed its numerous functions (heat transfer, fluidisation and reaction gaseous by-products removal) the gas is discharged from the reactor 101 passing through at first an inertial separator (for example, of the multi-plate type) and  
15 then a centrifugal separator (for example, a cyclone) 133, both suitable for separating the possible dragged "PET sand" particles.

The employed gas velocity is of 3 times with respect to the minimum fluidisation velocity for the first stage and 2 times  
20 with respect to the minimum fluidisation velocity for the stages from the 2<sup>nd</sup> to the 5<sup>th</sup>, this to create a higher vacuum degree in the first fluidised stage so to oppose the agglomeration tendency of the fed cold amorphous "PET sand", while for the stages from the 2<sup>nd</sup> to the 5<sup>th</sup>, having the "PET  
25 sand" crystallinity values gradually increasing (as a consequence of the maintaining at temperature), said

agglomeration risk is reduced.

The gas is nitrogen (purity: 99.99%) with a dew point of  $-45^{\circ}\text{C}$ . For the solid phase polycondensation test a "PET sand", formed by particles of 200  $\mu\text{m}$  size (more precisely: 99.9% < 220  $\mu\text{m}$  and  
5 0.1% < 180  $\mu\text{m}$ ) of amorphous PET containing 2.0% by weight of isophthalic acid and having a melting point of  $251^{\circ}\text{C}$ , has been employed.

The PET granules flow was of 250 kg/h; the overall hold-up of solid in the five stages (at the fluidisation conditions above-  
10 mentioned) was measured to be 360 kg (weigh of the "PET sand" mass contained in the five stages when stopping the gas feeding): it results an average residence time of the solid equal to 1 hour and 25 minutes (360 kg / 250 kg/h). The pre-polymer starting intrinsic viscosity was  $0.30 \pm 0.005$  dl/g; the  
15 acetaldehyde content was 47 p.p.m.; the PET granules temperature at the entrance of the reactor was  $23^{\circ}\text{C}$ .

The temperature of the gas fed to the five stages was  $228 \pm 0.5^{\circ}\text{C}$ .

The same "PET sand", after solid phase polymerisation, at the  
20 exit of the reactor had a final intrinsic viscosity of  $0.82 \pm 0.01$  dl/g.

#### Example 2

In this second carrying out example of the process according to the invention, all the conditions applied in the first example  
25 have been retained, with the exception of the fed gas temperature, which has been set as follows:

1<sup>st</sup> stage:  $228 \pm 0.5$  °C;

2<sup>nd</sup> stage:  $229 \pm 0.5$  °C;

3<sup>rd</sup> stage:  $229 \pm 0.5$  °C;

4<sup>th</sup> stage:  $230 \pm 0.5$  °C;

5 5<sup>th</sup> stage:  $230 \pm 0.5$  °C.

The "PET sand", after solid phase polymerisation, at the exit of the reactor had a final intrinsic viscosity of  $0.854 \pm 0.01$  dl/g.

### Example 3

10 In this third carrying out example of the process according to the invention, all the conditions applied in the first example have been retained, with the exception of the intrinsic viscosity of the fed amorphous "PET sand" and of the temperature of the gas fed to the five stages.

15 In particular, amorphous "PET sands" have been used having the following different intrinsic viscosity parameters:  $0.26 \pm 0.005$  dl/g;  $0.36 \pm 0.005$  dl/g;  $0.45 \pm 0.005$  dl/g;  $0.58 \pm 0.005$  dl/g. In all these tests the gas feeding temperature (gas temperature equal for the five stages) has been made to change,  
20 so as to achieve a final intrinsic viscosity of 0.82 dl/g for the "PET sand" after polymerisation.

Obviously, not having changed the feeding flow-rate of both the solid and the gas, the average residence time of the solid remained of 1 hour and 25 minutes.

25 The gas temperatures, to achieve the same solid phase polymerised PET final intrinsic viscosity of 0.82 dl/g for

starting from the four different "PET sands", have been respectively:  $229 \pm 0.5$  °C;  $225 \pm 0.5$  °C;  $218 \pm 0.5$  °C;  $211 \pm 0.5$  °C.

In each of the checked conditions, the final intrinsic  
5 viscosity variation have been noticed to be of  $\pm 0.01$  dl/g, corresponding to an increase of the final intrinsic viscosity variation due to solid phase polymerisation of  $\pm 0.005$  dl/g, this confirming the good "plug-flow" behaviour achieved on the solid phase in the serial multistage process.

10 It has to be noticed that in the conventional solid phase polymerisation processes, such as those carried out inside a cylindrical, with vertical axis, moving bed reactor, the increase of the final intrinsic viscosity variation due to solid phase polymerisation is of  $\pm 0.01 \div \pm 0.015$  dl/g.

15 The same test has been also performed in a conventional, cylindrical, vertical, moving bed reactor having an internal diameter of 1.6 meters, bed height of 8 meters and "PET sand" downhill velocity of 0.42 meters/hour.

The "PET sand", in this case, was previously crystallised to a  
20 degree of crystallinity  $X_c = 38\%$  so as to give proper flowability to the subsequent moving bed reactor, by heating and maintaining a temperature of 200°C for 5 minutes.

All the tests performed with this plant arrangement have highlighted a process threshold value of  $216 \pm 0.5$  °C, beyond  
25 which irreversible agglomeration phenomena among particles started to occur, this resulting in a progressive loss of

flowability.

Only with "PET sand" having initial I.V. of  $0.45 \pm 0.005$  dl/g and with the one having initial I.V. of  $0.58 \pm 0.005$  dl/g it was possible to solid phase polymerise, achieving a final I.V. of 0.82 dl/g.

In the first case the residence time was of 16 hours at a temperature of  $215 \pm 0.5$  °C and in the second one of 9.5 hours at a temperature of  $215 \pm 0.5$  °C.

The exposed example clearly shows that a conventional, cylindrical, vertical, moving bed reactor has a threshold maximum temperature as well as a limit to the intrinsic viscosity increase achievable by keeping unchanged the reactor, the bed height and velocity.

In this specific case, the allowed maximum temperature of the reactor was of about 215°C and the achievable maximum intrinsic viscosity increase was of about 0.37 dl/g ( $0.82$  final -  $0.45$  initial) with a bed reactor height of 8 meters and a velocity of 0.42 meters/hour.

From what above disclosed, it clearly results that the process according to the invention allows to achieve a higher PET molecular weight increase as well as to operate at a temperature significantly higher than those previously employed with the conventional moving bed processes, without agglomeration phenomena and other unwanted side effects and achieving a good result in terms of uniformity of the product final characteristics, thanks to the "plug-flow" behaviour on

the solid phase in the plurality of fluidised stages in series. Furthermore the invention will be advantageously applicable to any polyester which can be solid phase polymerised. The most common polyesters suitable for use in the invention have at least about 75 mole percent of their acid moieties provided by an aromatic dicarboxylic acid, such as terephthalic acid, isophthalic acid, or a naphthalenic dicarboxylic acid (preferably 2,6-) with the diol moieties provided by glycols such as ethylene glycol, butylene glycol, 1,4-dimethylol cyclohexane and the like or aromatic diols such as hydroquinone and catechol. Said polyesters can contain other dicarboxylic acids such as adipic acid, isophthalic acid, sebacic acid, and the like. Polyethylene terephthalate, polyethylene isophthalate, polyethylene naphthalate, and polybutylene terephthalate homopolymers are representative examples of such polyesters.

Blends of various polyesters can also be solid phase polymerised in the process according to the invention. The polyester pre-polymers (amorphous starting polyesters) utilised in this invention can be made in any manner but are typically prepared by conventional melt phase polymerisation techniques. These polyester pre-polymers have an initial starting IV of at least about 0.2 dl/g as measured in a 60:40 (by weight): phenol ÷ 1,1,2,2,-tetrachloroethane solvent system at a temperature of 30 °C. The rate at which polyethylene terephthalate pre-polymer can be solid state polymerised also depends on the carboxyl end



group (i.e.-COOH) content of the pre-polymer. Generally, pre-polymers having a carboxyl end group content within the range of about 18% to about 40% achieve maximum solid state polymerisation rates. It is preferred for such pre-polymers to have a carboxyl end group content within the range of about 24% to 33% (see for example US 4,238,593). Suitable polyester pre-polymers which can be solid state polymerised using my invention are comprised of one or more diacid components and one or more diol components. The diacid component in the polyesters are normally alkyl dicarboxylic acids which contain from 4 to 36 carbon atoms, diesters of alkyl dicarboxylic acids which contain from 6 to 38 carbon atoms, aryl dicarboxylic acids which contain from 8 to 20 carbon atoms, diesters of aryl dicarboxylic acids which contain from 10 to 22 carbon atoms, alkyl substituted aryl dicarboxylic acids which contain from 9 to 22 carbon atoms, or diesters of alkyl substituted aryl dicarboxylic acids which contain from 11 to 22 carbon atoms. The preferred alkyl dicarboxylic acids will contain from 4 to 12 carbon atoms. Some representative examples of such alkyl dicarboxylic acids include glutaric acid, adipic acid, pimelic acid, and the like. The preferred diesters of alkyl dicarboxylic acids will contain from 6 to 12 carbon atoms. A representative example of such a diester of an alkyl dicarboxylic acid is azelaic acid. The preferred aryl dicarboxylic acids contain from 8 to 16 carbon atoms. Some representative examples of aryl dicarboxylic acids are

terephthalic acid, isophthalic acid, and orthophthalic acid. The preferred diesters of aryl dicarboxylic acids contain from 10 to 18 carbon atoms. Some representative examples of diesters of aryl dicarboxylic acids include diethyl terephthalate, diethyl isophthalate, diethyl orthophthalate, dimethyl naphthalate, diethyl naphthalate and the like. The preferred alkyl substituted aryl dicarboxylic acids contain from 9 to 16 carbon atoms and the preferred diesters of alkyl substituted aryl dicarboxylic acids contain from 11 to 15 carbon atoms.

10 The diol component of the polyester pre-polymers is normally comprised of glycols containing from 2 to 12 carbon atoms, glycol ethers containing from 4 to 12 carbon atoms, and polyether glycols having the structural formula  $\text{HO}-(\text{A}-\text{O})_n-\text{H}$  wherein A is an alkylene group containing from 2 to 6 carbon atoms and wherein n is an integer from 2 to 400. Generally, 15 such polyether glycols will have a molecular weight of 400 to about 4000. Preferred glycols normally contain from 2 to 8 carbon atoms and more preferably from 4 to 8 carbon atoms. Some representative examples of glycols that can be utilised as the 20 diol component include ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 2,2-diethyl-1,3-propane diol, 2,2-dimethyl-1,3-propane diol, 2-butyl-1,3-propane diol, 2-ethyl-2-isobutyl-1,3-propane diol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 2,2,4-trimethyl-1,6-hexane 25 diol, 1,3-cyclohexane dimethanol, 1,4-cyclohexane dimethanol, and 2,2,4,4-tetramethyl-1,3-cyclobutane diol. Some

representative examples of polyether glycols that can be used include polytetramethylene glycol and polyethylene glycol.

Branched polyester pre-polymers can also be solid state polymerised in the process of the present invention. Such

5 branched polyesters normally contain branching agents which have three or more functional groups and preferably three or four functional groups. Reactive functional groups can be carboxyl groups or aliphatic hydroxyl groups. The branching agent utilised in such branched polyesters can optionally  
10 contain both carboxyl groups and hydroxyl groups. Examples of acidic branching agents include trimesic acid, trimellitic acid, pyromellitic acid, butane tetracarboxylic acid, naphthalene tricarboxylic acids, and cyclohexane-1,3,5-tricarboxylic acids. Some representative examples of hydroxyl  
15 branching agents (polyols) include glycerin, trimethylol propane, pentaerythritol, dipentaerythritol, 1,2,6-hexane triol, and 1,3,5-trimethylol benzene. Generally, from 0 to 3 percent of a polyol containing from 3 to 12 carbon atoms will be used as the branching agent (based upon the total diol  
20 component).

High strength polyesters which utilise at least one bis-hydroxyalkyl pyromellitic diimide in their diol component can also be solid state polymerised. The diol component in these polyesters will normally contain from 5 to 50 mole percent of  
25 one or more bis-hydroxyalkyl pyromellitic diimides and will preferably be comprised of from 10 to 25 mole percent of at

least one bis-hydroxyalkyl pyromellitic diimide. The remaining portion of the diol component is comprised of additional copolymerisable diols.

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## CLAIMS

1. A reactor (101;301) for solid phase continuous polymerisation of polyethylene terephthalate (PET), comprising:

- a casing (103;303);

5 - a feeding line (111;311) to feed a low molecular weight PET pre-polymers flow into said reactor (101;301);

- a gas line (121;321) to feed, through supply valves (123;323), a gas into said reactor (101;301);

10 - a discharging line (141;341) inferiorly connected to the bottom of the reactor (101;301) to discharge the polymerised product;

- a circuit (131;331) connected to the reactor (101;301) to purify the gas and to recover pre-polymer particles by means of a proper separator (133;333),

15 characterised in that inside said reactor (101;301) means are provided to generate a plurality of fluidised stages in series (109;309) to cause an increase of the intrinsic viscosity (I.V.) of said PET pre-polymers flow.

2. A reactor according to claim 1, characterised in that said casing (103) of said reactor (101) has a substantially parallelepiped shape and it is horizontally arranged.

3. A reactor according to claim 2, characterised in that said means comprise a plurality of inferior vertical walls (105a) secured to the base (107a) of said reactor (101) and a  
25 plurality of superior vertical walls (105b) secured to the ceiling (107b) of said reactor (101), between said inferior

walls being generated said fluidised stages (109).

4. A reactor according to claim 3, characterised in that said supply valves (123) are in such a number and arranged in such a way to generate a sufficient gas flow in correspondence with  
5 each fluidised stage (109).

5. A reactor according to claim 4, characterised in that said supply valves (123) associated to the same fluidised stage (109) are equipped with heating devices (125) suitable for bringing at the desired temperature the inert gas flowing  
10 through the bottom (104) of the reactor (101) in correspondence with each fluidised stage (109), this way achieving a differentiated heating of said fluidised stages (109).

6. A reactor according to claim 1, characterised in that said casing (303) of said reactor (301) has a substantially  
15 cylindrical shape and it is vertically arranged.

7. A reactor according to claim 6, characterised in that said means comprise a plurality of shelves (305) secured to the internal wall (307) of said casing (303) in correspondence with which said fluidised stages (309) are generated.

20 8. A reactor according to claim 7, characterised in that said shelves (305), provided inside said casing (303), are secured to said internal wall (307) of said casing (303) so to radially extend, up to about the centre line of the chamber created inside said casing (303).

25 9. A reactor according to claim 8, characterised in that said shelves (305) are preferably formed from holed metal plates.

10. A reactor according to claim 9, characterised in that said shelves (305), provided inside said casing (303), are almost horizontal.

11. A reactor according to claim 10, characterised in that  
5 said shelves (305) are alternately arranged so to define an obligatory path inside said reactor (301) for the pre-polymers descending flow.

12. A reactor according to any of the preceding claims,  
characterised in that said fluidised stages in series (109;309)  
10 are in a number of five.

13. A reactor according to claim 1, wherein said feeding line (111;311) is equipped with a device (113;313) suitable for regulating the flow-rate of fed amorphous PET pre-polymer and to prevent gas leakage.

14. A reactor according to claim 13, wherein said device (113;313) is a rotating volumetric distributing apparatus.

15. A reactor according to claim 1, wherein said discharging line (141;341) is equipped with a device (143;343) suitable for discharging the PET after solid phase polymerisation and to  
20 prevent gas leakage.

16. A reactor according to claim 15, wherein said device (143;343) is a rotating volumetric distributing apparatus.

17. A reactor according to claim 1, wherein said circuit (131;331) further comprises a separation device (135;335) to  
25 recover ethylene glycol and oligomers at the liquid state and then to recycle them upstream the overall PET manufacturing

cycle.

18. A reactor according to any of the preceding claims, characterised in that said PET pre-polymers flow has a low initial I.V. value, generally an I.V. value in the range of  
5 0.20 ÷ 0.45 dl/g and preferably an I.V. value of 0.30 dl/g.

19. A reactor according to any of the preceding claims, characterised in that said I.V. increase of said PET pre-polymers flow is comprised in the range of 0.35 ÷ 0.65 dl/g, preferably of 0.55 dl/g.

10 20. A reactor according to any of the preceding claims, characterised in that said I.V. increase of said PET pre-polymers flow is  $\geq 0.06$  dl/g.

21. A reactor according to any of the preceding claims, characterised in that said I.V. increase of said PET pre-  
15 polymers flow is  $\geq 0.20$  dl/g.

22. A reactor according to any of the preceding claims, characterised in that said PET pre-polymers flow is a PET sand flow, being the sand particle size preferably comprised in the range 60 ÷ 300  $\mu\text{m}$ .

20 23. A reactor according to any of the preceding claims, characterised in that said PET pre-polymers flow is a PET sand flow, being the sand particle size preferably comprised in the range 100 ÷ 250  $\mu\text{m}$ .

24. A reactor according to any of the preceding claims,  
25 characterised in that said PET pre-polymers flow fed into the reactor (101;301) is maintained in said reactor (101;301) at a



temperature comprised in the range  $200 \div 235$  °C, preferably of 230°C.

25. A reactor according to any of the preceding claims, characterised in that said PET pre-polymers flow fed into the reactor (101;301) is maintained in said reactor (101;301) at a temperature comprised in the range  $205 \div 230$  °C.

26. A reactor according to any of the preceding claims, characterised in that said gas is an inert gas, preferably nitrogen.

27. A reactor according to any of the preceding claims, wherein said gas flow inside said reactor is directed in cross-flow or in counter-current flow with respect to the flow of the PET granules that pass through said reactor.

28. A reactor according to any of the preceding claims, wherein the ratio between the mass of the gas flow that passes through said reactor and the mass of the PET granules in the reactor is  $> 0.62$ .

29. A reactor according to any of the preceding claims, wherein the ratio between the mass of the gas flow that passes through said reactor and the mass of the PET granules in the reactor is  $> 0.9$ .

30. A reactor according to any of the preceding claims, wherein said gas is an inert gas or air.

31. A reactor according to claim 30, wherein said gas is air with a dew point  $< -30$ °C.

32. A reactor according to claim 30, wherein said gas is a

mixture of gases chosen from the group comprising nitrogen, noble gases, carbon dioxide, carbon monoxide and oxygen and wherein the oxygen content is < 10% by weight.

33. A reactor according to claim 30, wherein said gas is a  
5 mixture of gases chosen from the group comprising nitrogen, noble gases, carbon dioxide, carbon monoxide and oxygen and wherein the oxygen content is < 6% by weight.

34. A reactor according to any of the preceding claims, wherein the gas is recycled to the reactor, after having been  
10 purified of the organic impurities, until a level of organic impurities  $\leq 100$  p.p.m. by weight ( $\text{CH}_4$  equivalent) has been reached.

35. A reactor according to any of the preceding claims, wherein the PET granules have an irregular shape with a volume  
15 comprised between  $0.05$  and  $10 \text{ mm}^3$ .

36. A reactor according to any of the preceding claims, wherein inside said reactor the polyester granules are subjected to a solid phase polycondensation and/or drying and/or crystallisation and/or dealdehydisation.

20 37. A process for solid phase continuous polymerisation of polyethylene terephthalate (PET), comprising the steps of:

- feeding a low molecular weight PET pre-polymers flow into a reactor (101;301) through a feeding line (111;311);
- feeding a gas into said reactor (101;301) through a gas  
25 line (121;321) in cross-flow or in counter-current flow with respect to said PET pre-polymers flow,

characterised in that said polymerisation is carried out in a plurality of fluidised stages in series (109;309) generated inside said reactor (101;301) to cause an increase of the intrinsic viscosity (I.V.) of said PET pre-polymers flow.

5 38. A process according to claim 37, characterised in that said polymerisation is carried out in a number of fluidised stages in series (109;309) of five.

39. A process according to claim 38, characterised in that said polymerisation is carried out at non-isothermal  
10 conditions.

40. A process according to claim 38, characterised in that said polymerisation is carried out at isothermal conditions.

41. A process according to claim 38, characterised in that said polymerisation is carried out in a time period preferably  
15 of about 2 hours.

42. A process according to any of the claims from 37 to 41, characterised in that said PET pre-polymers flow has a low initial I.V. value, generally an I.V. value in the range of 0.20 ÷ 0.45 dl/g and preferably an I.V. value of 0.30 dl/g.

20 43. A process according to any of the claims from 37 to 42, characterised in that said I.V. increase of said PET pre-polymers flow is comprised in the range of 0.35 ÷ 0.65 dl/g, preferably of 0.55 dl/g.

44. A process according to any of the claims from 37 to 43,  
25 characterised in that said I.V. increase of said PET pre-polymers flow is  $\geq 0.06$  dl/g.

45. A process according to any of the claims from 37 to 44, characterised in that said I.V. increase of said PET pre-polymers flow is  $\geq 0.20$  dl/g.

46. A process according to any of the claims from 37 to 45,  
5 characterised in that said PET pre-polymers flow is a PET sand flow, being the sand particle size preferably comprised in the range  $60 \div 300$   $\mu\text{m}$ .

47. A process according to any of the claims from 37 to 46,  
characterised in that said PET pre-polymers flow is a PET sand  
10 flow, being the sand particle size preferably comprised in the range  $100 \div 250$   $\mu\text{m}$ .

48. A process according to any of the claims from 37 to 47,  
characterised in that said PET pre-polymers flow fed into the reactor (101;301) is maintained in said reactor (101;301) at a  
15 temperature comprised in the range  $200 \div 235$   $^{\circ}\text{C}$ , preferably at  $230^{\circ}\text{C}$ .

49. A process according to any of the claims from 37 to 48,  
characterised in that said PET pre-polymers flow fed into the reactor (101;301) is maintained in said reactor (101;301) at a  
20 temperature comprised in the range  $205 \div 230$   $^{\circ}\text{C}$ .

50. A process according to any of the claims from 37 to 49,  
characterised in that said gas is an inert gas, preferably nitrogen.

51. A process according to any of the claims from 37 to 50,  
25 wherein said gas flow inside said reactor is directed in cross-flow or in counter-current flow with respect to the flow of

said PET granules that pass through said reactor.

52. A process according to any of the claims from 37 to 51,  
wherein the ratio between the mass of the gas flow that passes  
through the reactor and the mass of the PET granules in the  
5 reactor is  $> 0.62$ .

53. A process according to any of the claims from 37 to 52,  
wherein the ratio between the mass of the gas flow that passes  
through the reactor and the mass of the PET granules in the  
reactor is  $> 0.9$ .

10 54. A process according to any of the claims from 37 to 53,  
wherein said gas is an inert gas or air.

55. A process according to claim 54, wherein said gas is air  
with a dew point  $< -30^{\circ}\text{C}$ .

56. A process according to claim 54, wherein said gas is a  
15 mixture of gases chosen from the group comprising nitrogen,  
noble gases, carbon dioxide, carbon monoxide and oxygen and  
wherein the oxygen content is  $< 10\%$  by weight.

57. A process according to claim 54, wherein said gas is a  
mixture of gases chosen from the group comprising nitrogen,  
20 noble gases, carbon dioxide, carbon monoxide and oxygen and  
wherein the oxygen content is  $< 6\%$  by weight.

58. A process according to any of the claims from 37 to 57,  
wherein the gas is recycled to the reactor, after having been  
purified of the organic impurities, until a level of organic  
25 impurities  $\leq 100$  p.p.m. by weight ( $\text{CH}_4$  equivalent) has been  
reached.

59. A process according to any of the claims from 37 to 58, wherein the PET granules have an irregular shape with a volume comprised between 0.05 and 10 mm<sup>3</sup>.

60. A process according to any of the claims from 37 to 59,  
5 wherein inside said reactor the polyester granules are subjected to a solid phase polycondensation and/or drying and/or crystallisation and/or dealdehydisation.

61. A process according to any of the claims from 37 to 60, characterised in that ethylene glycol and oligomers present at  
10 the end of said polymerisation are recovered at the liquid state in a separation device (135;335) provided in a circuit (131;331) connected to the reactor (101;301) and then recycled upstream the overall PET manufacturing cycle.

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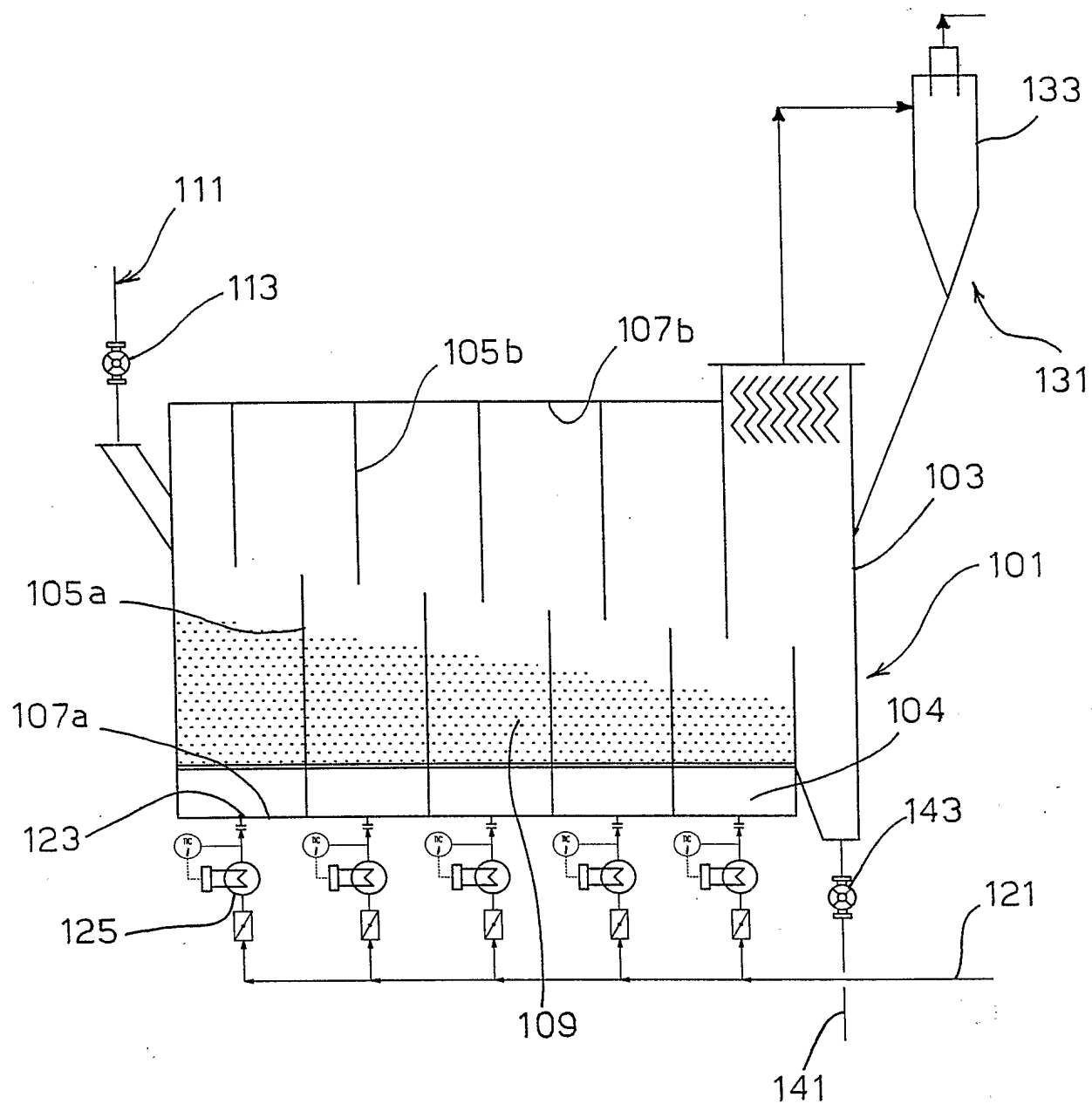
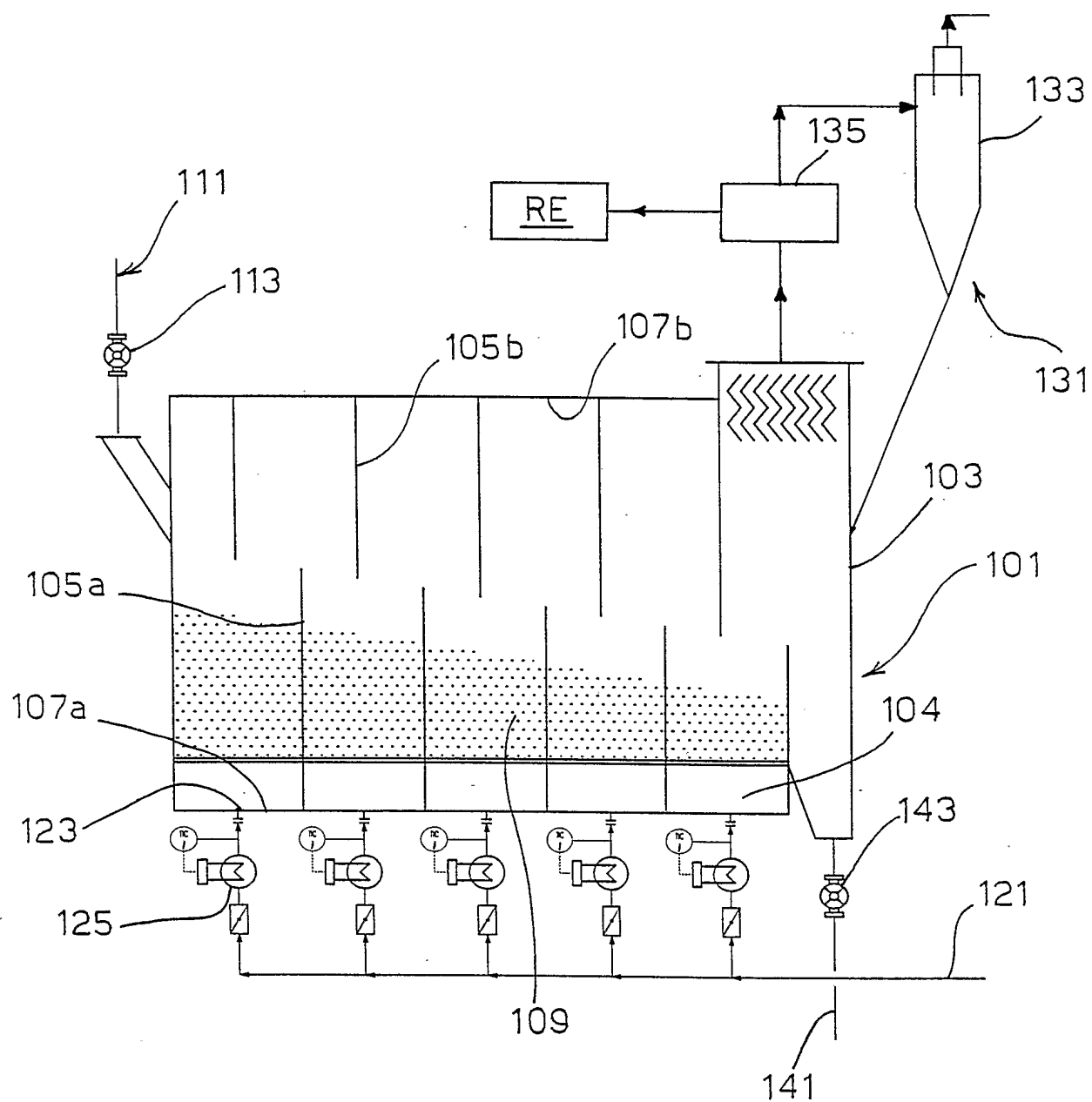


FIG. 1A

**FIG. 1B**



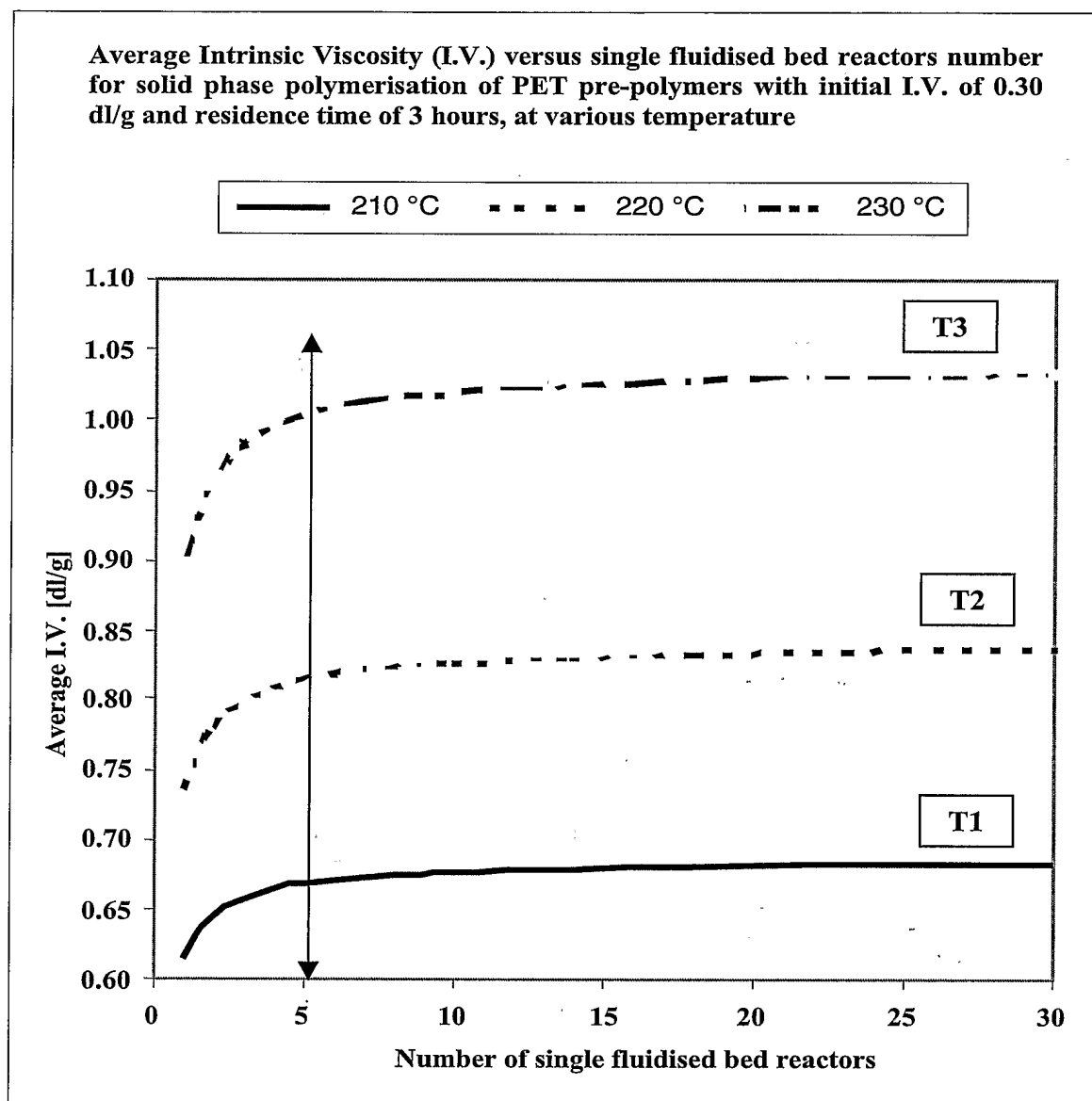


FIG. 2A

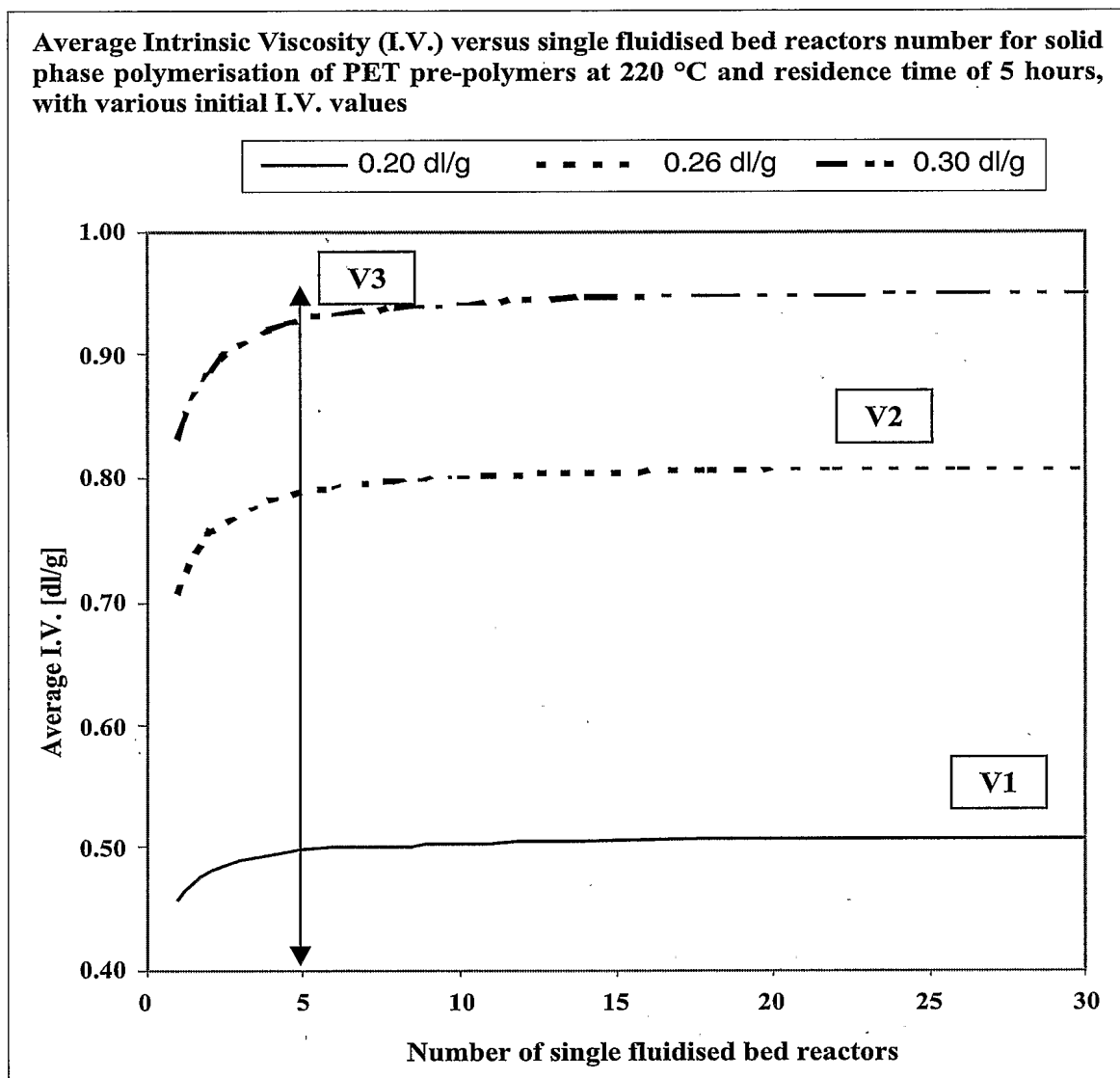


FIG. 2B

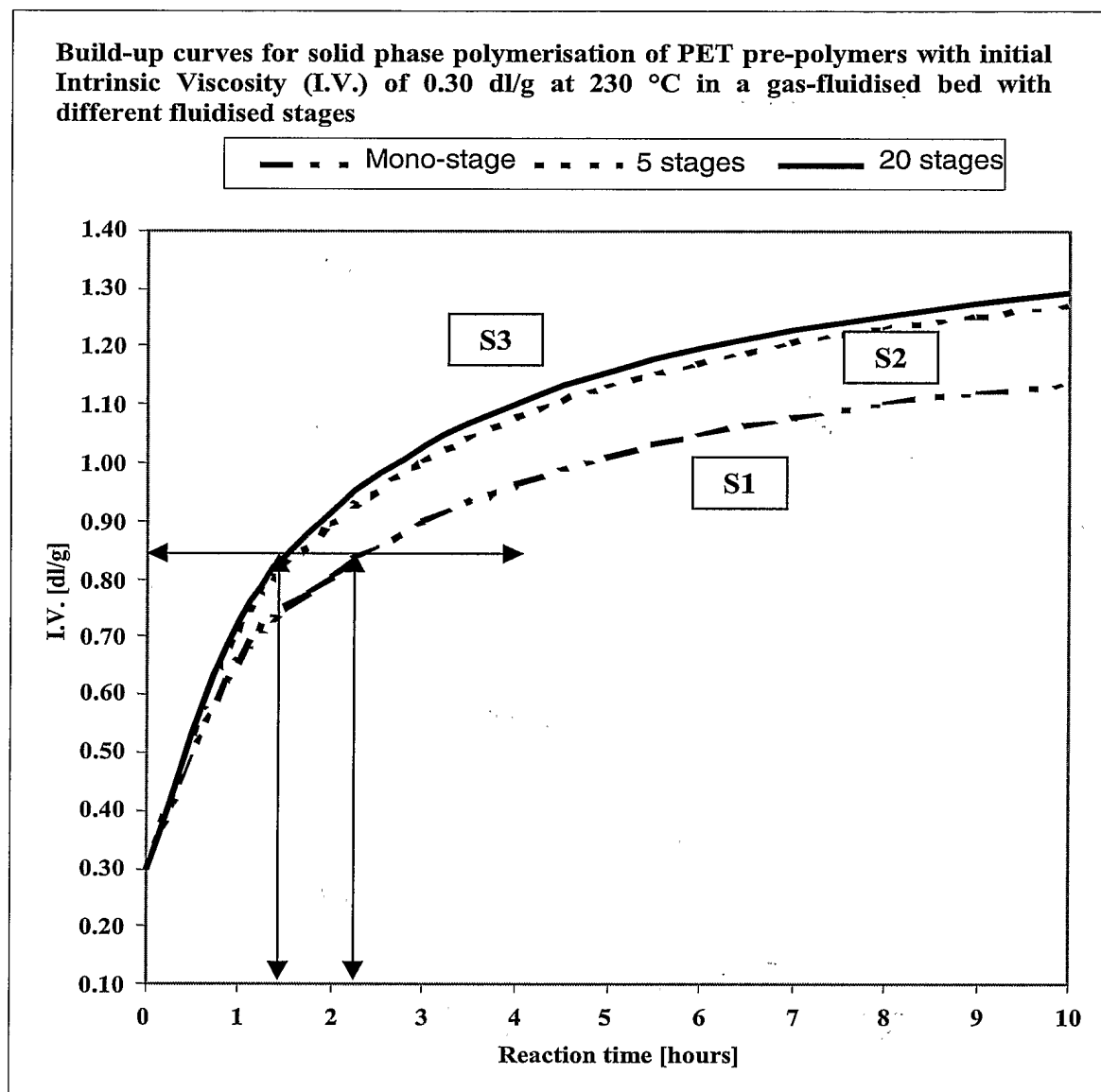


FIG. 2C

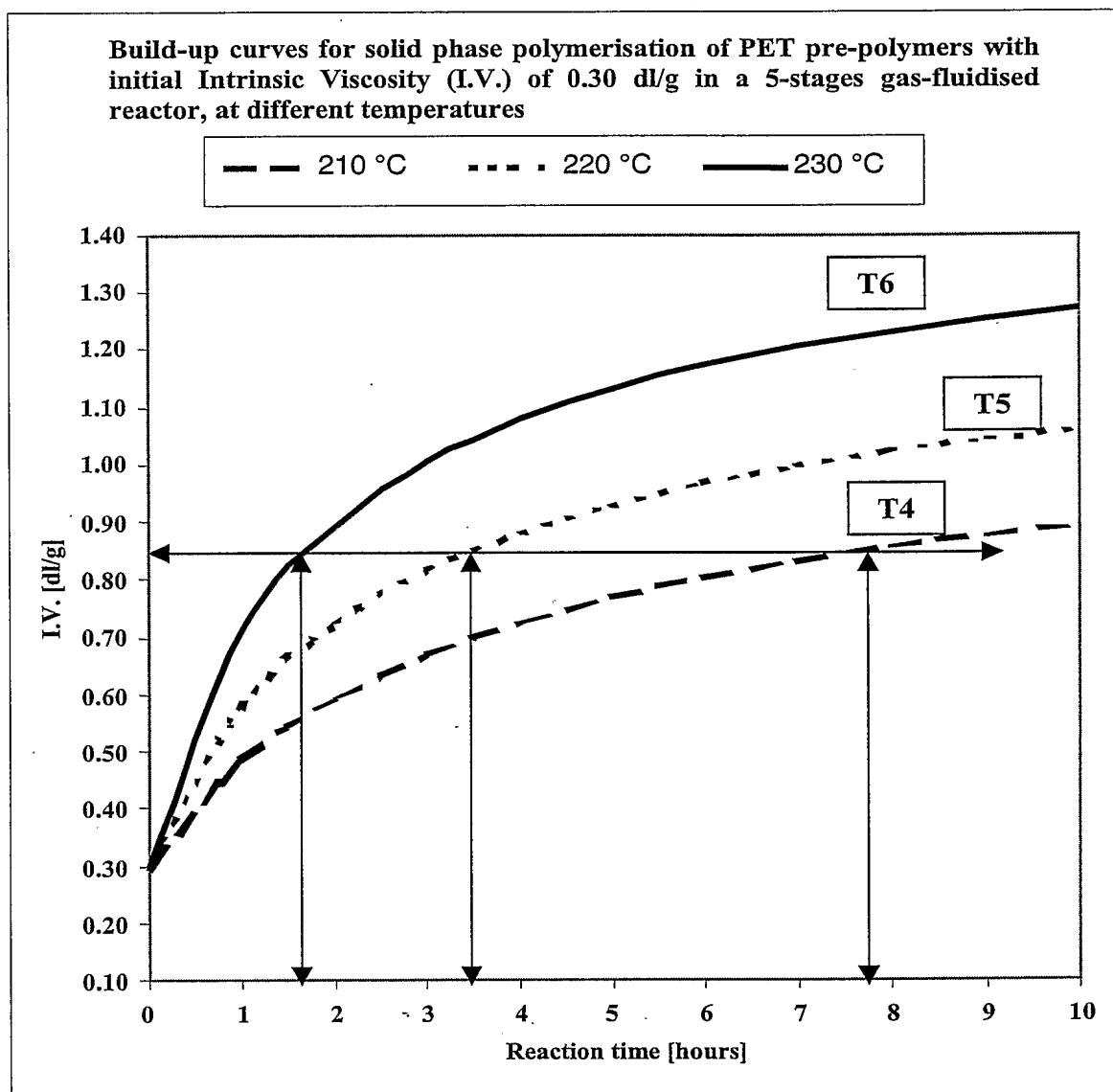
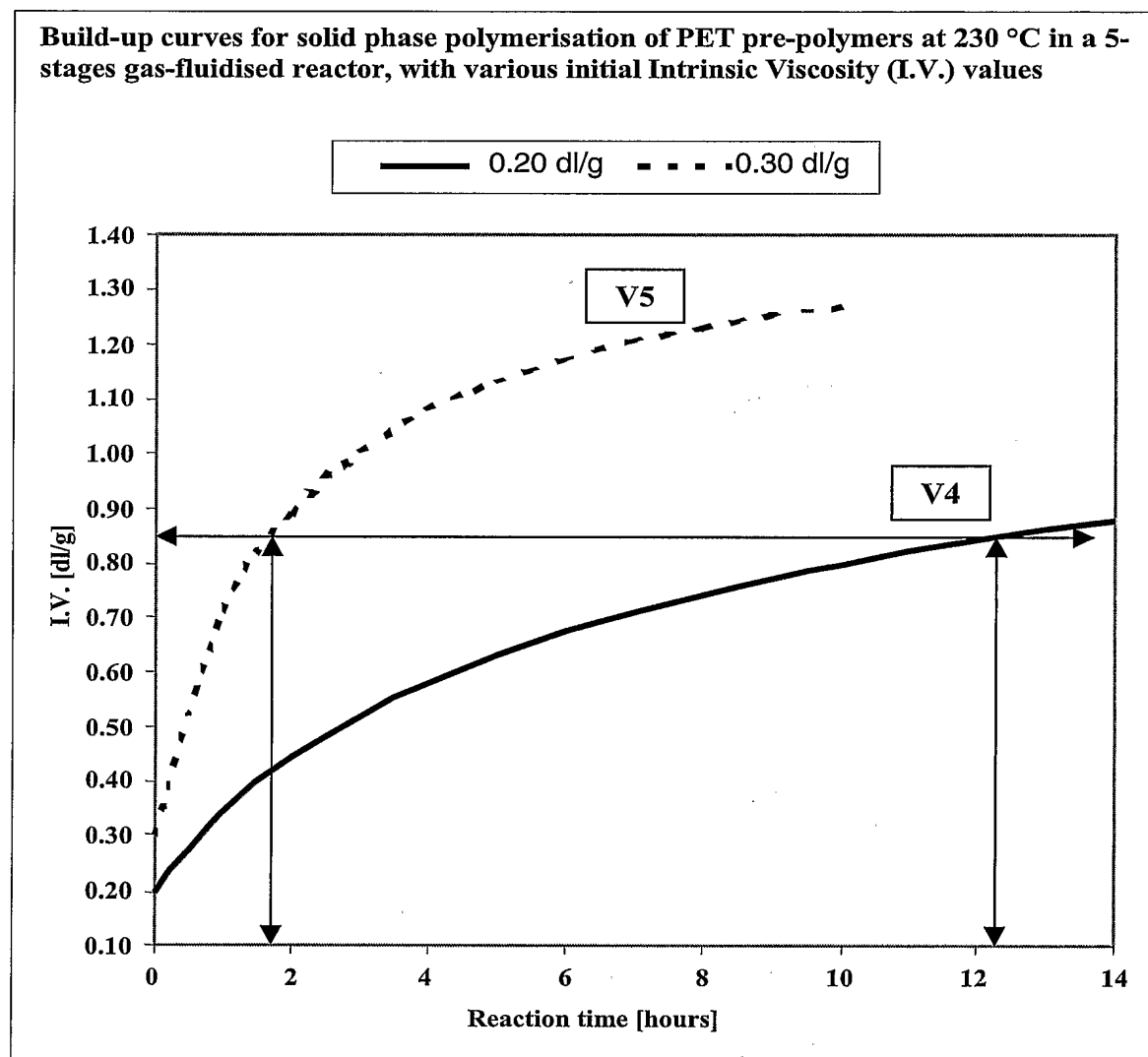
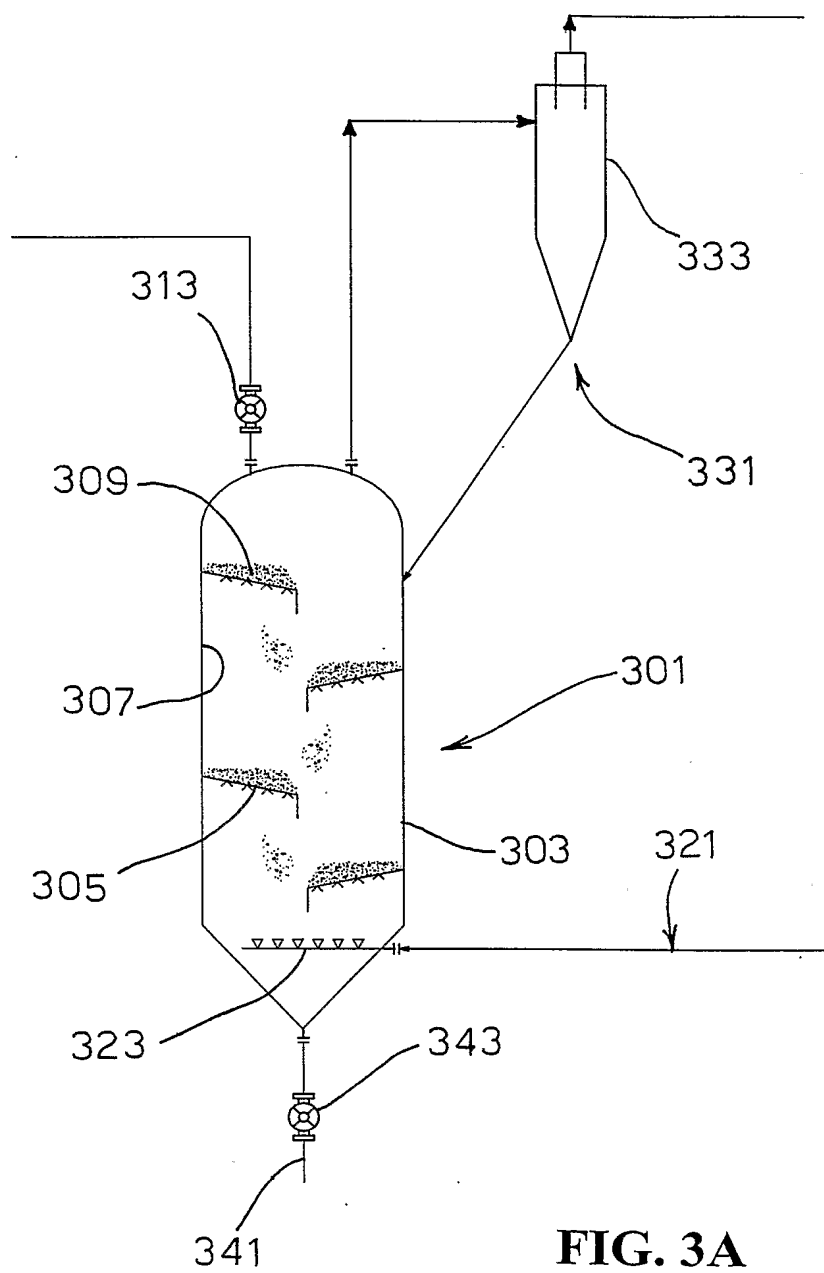
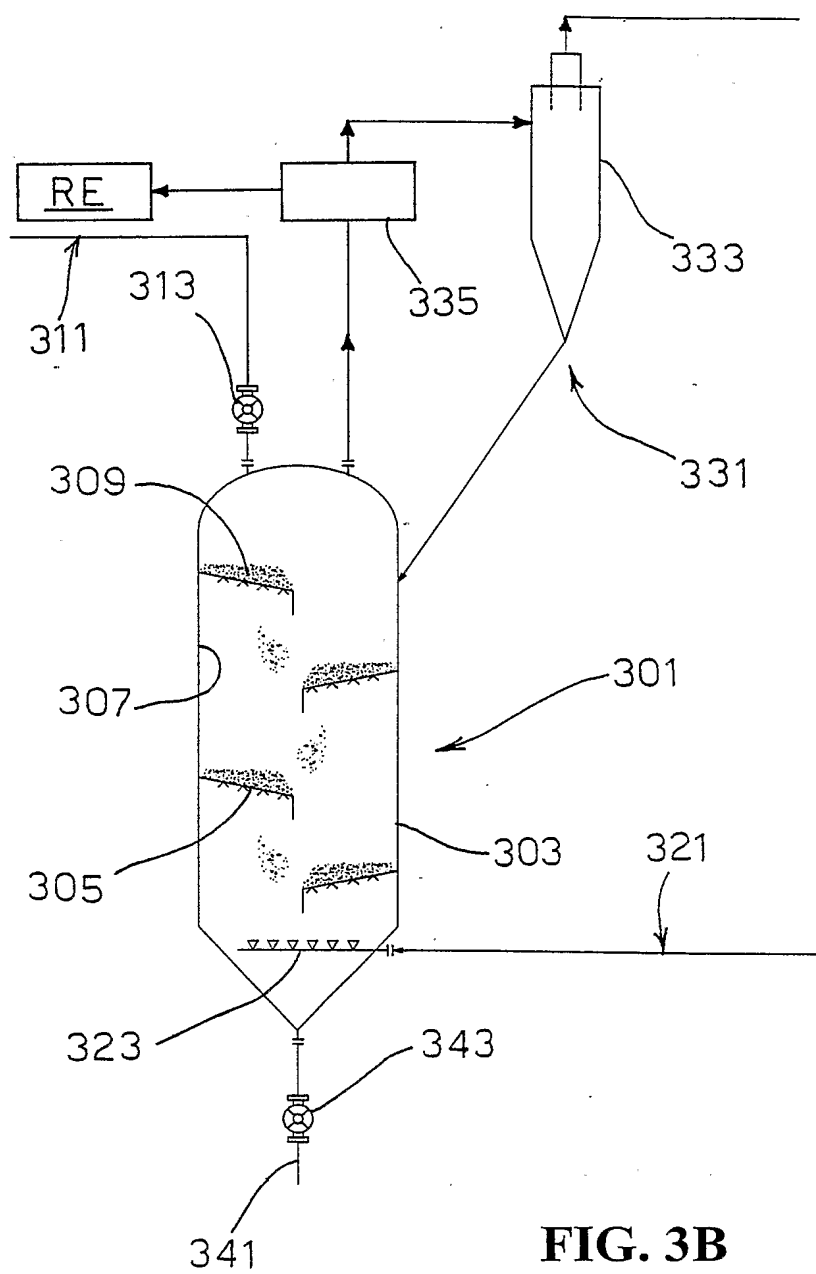


FIG. 2D

**FIG. 2E**





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/11181

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G63/80 B01J19/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 169 913 A (STAFFIN H KENNETH ET AL) 8 December 1992 (1992-12-08) claims 1,6,8,10 column 5, paragraph 4 ---	1-4, 15, 26, 27
X, Y	US 3 330 809 A (COFFEE ROBERT D ET AL) 11 July 1967 (1967-07-11)  claims 1-16 column 4, line 59 - column 9, line 73 ---	1, 6-10, 13, 15, 17, 37, 39, 43-51, 54, 60, 61
A	GB 1 282 030 A (RHODIACETA) 19 July 1972 (1972-07-19) claims 1, 6; figures 1, 4 page 3, column 1, line 6 - line 17 --- -/-	1, 6, 11



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

6 February 2004

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/11181

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 440 019 A (SCHELLER HANS ET AL) 22 April 1969 (1969-04-22) figure 1 column 3, paragraph 1 ---	1,2
X	EP 0 712 703 A (SINCO ENG SPA) 22 May 1996 (1996-05-22) claims 1,7,10 figure 1 page 2, line 35 - line 40 page 3, line 56 - line 57 ---	1,2,36
Y	DATABASE WPI Week 7422 Derwent Publications Ltd., London, GB; AN 1974-40918v XP002269310 & JP 49 018177 A (TEIJIN), 8 May 1974 (1974-05-08) abstract -----	1,6-10, 13,15, 17,37, 39, 43-51, 54,60,61

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/11181

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5169913	A	08-12-1992	US 5378434 A	03-01-1995
US 3330809	A	11-07-1967	DE 1243389 B	29-06-1967
			FR 1360765 A	15-05-1964
			GB 1041853 A	07-09-1966
GB 1282030	A	19-07-1972	BE 742200 A	25-05-1970
			CH 498888 A	15-11-1970
			DE 1959455 A1	11-06-1970
			FR 1593419 A	25-05-1970
			LU 59878 A1	27-05-1970
			NL 6917332 A	28-05-1970
US 3440019	A	22-04-1969	AT 270230 B	25-04-1969
			DE 1645630 A1	11-02-1971
			FR 1482308 A	26-05-1967
			GB 1114477 A	22-05-1968
			NL 6607576 A , B	02-12-1966
EP 0712703	A	22-05-1996	IT MI942355 A1	20-02-1995
			AU 688978 B2	19-03-1998
			AU 3666195 A	30-05-1996
			CA 2162233 A1	22-05-1996
			CN 1133309 A , B	16-10-1996
			DE 69525132 D1	14-03-2002
			DE 69525132 T2	22-08-2002
			EP 0712703 A2	22-05-1996
			ES 2169740 T3	16-07-2002
			JP 2971792 B2	08-11-1999
			JP 8225637 A	03-09-1996
			KR 201668 B1	15-06-1999
			PL 311408 A1	27-05-1996
			US 5714571 A	03-02-1998
JP 49018177	A	18-02-1974	NONE	